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(54) Article comprising conductive polymers and process for making the same.

(57) Polyamides comprising substantial amounts of Nylon-11 and/or Nylon-12 units are cross-linked by irradiation in the presence of an unsaturated cross-linking agent, preferably triallyl isocyanurate. The cross-linked products are particularly useful in the form of heat-recoverable shaped articles, eg. heat-shrinkable tubing.

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Cross-linking agents for use in this invention usually consist of elements selected from carbon, hydrogen, oxygen and nitrogen. The preferred cross-linking agent is triallyl isocyanurate, which we have found to give particularly good results even when used in small amounts and at low radiation doses. Triallyl cyanurate is also very useful, especially when used under conditions which cause isomerisation to the isocyanurate. Mixtures of cross-linking agents can be used. The amount of cross-linking agent used is preferably less than 4%, eg. 0.1 to 4%, particularly less than 2%, eg. 0.1 to 2%, especially about 1%, eg. 0.3 to 1.25%, based on the polymer component.

The polymeric composition may contain other ingredients in addition to the polymer component and the cross-linking agent (or residue thereof after radiation cross-linking). For example the composition may contain organic and/or inorganic flame retardants, fillers, processing aids and antioxidants. The amount of such additives may be for example up to 60% by weight of the composition, eg. 10 to 40%. Care should be taken to avoid the use of excessive amounts of antioxidants and other additives which inhibit cross-linking and make it necessary to use larger amounts of cross-linking agent and/or higher radiation dosages. It is an additional surprising feature of this invention that even compositions containing relatively large amounts of antioxidant, eg. 1 to 3% of the composition, can be successfully cross-linked.

We have found that excellent results can be obtained using radiation dosages of at most 12 Mrad, and often less, eg. at most 8 Mrad or at most 6 Mrad. In order to obtain a particular degree of cross-linking, the radiation dose required is dependent on the amount and type of cross-linking agent present. The cross-linking agent and radiation dose are selected so that the cross-linked article has an M_{100} value above its melting point, of at least 2.1 kg/cm^2, generally 2.1 to 10.5 kg/cm^2, preferably 2.6 to 4.2 kg/cm^2, and/or an E_{30} value above its melting point, of at least 5.6 kg/cm^2, preferably 5.6 to 17.5 kg/cm^2. The M_{100} and E_{30} values referred to herein are measured by a modulus test carried out at an elevated temperature above the melting point of the article, i.e. after melting is completed and, if the article is heat-recoverable, after it has been heat-recovered in the absence of any restraint. In this test, the stress required to elongate a specimen of the cross-linked article by 30 and 100% is measured, using an Instron tester at a crosshead speed of 5.1 cm (2 inch) /minute, a jaw separation of 4.8 cm (1.9 inch) and a chart speed of 12.7 cm (5 inch)/minute. A specimen, usually a strip 0.6 or 1.27 cm (0.25 or 0.5 inch) wide, cut from the cross-linked article is clamped at the top and allowed to equilibrate at the elevated temperature, and the lower end is then clamped. The force required to elongate the specimen to 30% and to 100% is recorded. The E_{30} and M_{100} values are then calculated as follows

$$E_{30} = \frac{\text{Force at 30\% elongation}}{\text{Initial cross-sectional area of specimen}} \times \frac{1.30}{0.30}$$

$$M_{100} = \frac{\text{Force at 100\% elongation}}{\text{Initial cross-sectional area of specimen}}$$

CLAIMS

1. An article, especially a heat-recoverable article, composed of a radiation cross-linked polymeric composition which

(a) has been cross-linked by radiation in the presence of an unsaturated radiation cross-linking agent,

(b) has an M_{100} value above its melting point of at least 2.1 kg/cm^2, preferably 2.1 to 10.5 kg/cm^2, particularly 2.6 to 4.2 kg/cm^2, and

(c) comprises a cross-linked organic polymer component which comprises at least 80%, preferably substantially 100%, by weight of at least one polyamide consisting essentially of monomer units which are linked to each other through amide linkages, at least 25%, preferably at least 75%, by weight of the monomer units having the formula

$$- NH - (CH_2)_p - CO -$$

where p is 11 or 12.

2. An article according to Claim 1 wherein the polymer component consists essentially of 75 to 100% by weight of Nylon-11 or Nylon-12 or a mixture thereof and 0 to 25% by weight of Nylon-6, Nylon-6,6, Nylon 6,9, Nylon 6,10, or Nylon 6,12 or a blend of two or more of these.

3. An article according to Claim 1 or 2 which is hollow and heat-shrinkable and which has a coating on its inner surface of a material which flows at the recovery temperature of the article.

7. A process according to Claim 4, 5 or 6 wherein the amount of said cross-linking agent is less than 4%, preferably less than 2%, by weight, based on the weight of the organic polymer component.

8. A process according to Claim 7 wherein the shaped article is irradiated to a dose of at most 12 Mrad, preferably at most 8 Mrad.

9. A process according to any one of claims 4 to 8 which further comprises the steps of

(3) heating the cross-linked article above its melting point;

(4) deforming the article while it is at a temperature above its melting point; and

(5) cooling the article while it is in the deformed condition;

whereby a heat-recoverable article is prepared.

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